

## **AN EFFECTIVE CB MATERIAL FROM COMBINED COMPONENTS OF TRIOSYN® RESIN AND SURFACE ENHANCED CARBON**

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### **ABSTRACT**

The tremendous concern over the threat of biological and chemical warfare agents has necessitated the research and development of greatly improved methods for the absorption and catalytic destruction of these toxic contaminants. With the use of proven biocidal efficiency of the Triosyn® iodine resin and carbon based new materials, the research objective is to produce a barrier possessing the dual properties of decontaminating both chemical warfare and biological agents. Vapor testing performed allowed for the down selection of prototypes; POX3/1/0/A, OX5H/C, and OX5H/D which displayed excellent absorption capacity, microbiological reduction rates greater than 99.9% against MS2 phage, and displayed non-toxic threshold limit values.

### **INTRODUCTION**

Triosyn® resins have been proven to kill on contact the most difficult bacterial spores, viruses, protozoa, parasites and fungi. Acute toxicology studies have shown no harmful or lethal dosage associated with exposure to the Triosyn® polymer. Triosyn® harnesses the power of iodine through the nontoxic application of demand release polymer technologies. The resin incorporates  $I^{-3}$  iodine, releases molecular  $I_2$  upon contact with a microorganism through ionic transfer devitalizing the microorganisms surface proteins.

Prototype generation: In order to achieve an adequate balance of the properties of CB materials, the carbon's adsorption capacity must be increased by enhancing carbon's chemisorption of compounds, which contain oxygen, chlorine, sulfur and phosphorus<sup>1</sup>. The presence of surface bound oxygen and hydrogen on carbon exercise a profound influence on the surface characteristics such as absorption of polar and non-polar gases and vapors. Surface bound molecular oxygen is formed on activated carbon when they are treated with different oxidizing agents using various synthetic techniques. As a result, carbon's capacity for toxic vapor removal does not simply depend on the surface area of the activated carbon but on the number of oxygen

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atoms in and on the carbon surface<sup>2</sup>. For a spherical activated carbon such as the NATO standard carbon (Ambersorb 572), the adsorbate molecule (methyl salicylate) must pass through the macro and transitional pores to the absorption site in the micropores. The absorption of MeS in the large cavities of the macropores is more readily susceptible to desorption of MeS and the subsequent transfer out through the material, than if the vapor molecule were to be absorbed by the micropores. By oxidizing the interstices and surface sites of carbon, one is essentially tailoring the size of the macropores by introducing chemisorbed oxygen groups within and on the carbon surface, thus reducing the pore size. Fixation of the acidic groups on the surface of the activated carbon not only affects the surface area and pore texture but it also produces a more hydrophilic surface<sup>3456</sup>. As a result, the surface-bound oxygen groups can also enhance the absorption capacity of MeS, which contains an electronegative methyl-ester and hydroxyl functional groups, through inter-molecular hydrogen bonding between the surface oxide groups of carbon and the hydroxyl functionality of the vaporized simulant. Conventional metal oxides such as alumina, possess reactivity toward chemical warfare simulants, subsequently, absorption is enhanced by the addition by impregnation of the nanosized inorganic oxide particles, which also served to increase the basicity of the carbon surface. The increase in absorption is most probably due to the larger surface area of the smaller oxide particles<sup>789</sup>. A merger of the above synthetic methodologies has resulted in a new class of prototypes represented under the heading of combined technologies.

## EXPERIMENTAL METHODS

Vapor testing: Among the tests conducted on canisters and textiles, is the service-life or gas-life which is a measure of the capacity for the removal of toxic contaminants. Our research assessed the service-life of the carbon/Triosyn® materials' capacity for absorbing methyl salicylate (MeS). MeS was selected as a surrogate since it exhibits similar physical properties to the mustard chemical warfare agent (HD)<sup>10</sup> i.e. it exhibits similar vapor pressure and water solubility, as well as low toxicity and the ability to be easily detected by analytical methods. It is the approved simulant used in CRDC-SP-84010 and EATM 311-3 testing. MeS (99+% purity) was purchased from Aldrich (product# 24,082-6, CAS# 119-36-8) and was used as received. The vapor testing apparatus contains the following three major sections: (1) a challenge gas mixture generator to provide a constant challenge gas flow rate and concentration, (2) a sample chamber to house the test prototypes, and (3) a detection system to continuously measure and record the concentration of the challenge vapor in the effluent stream.

A polydispersed aerosol vapor of MeS solution is generated using a 6-jet collision nebulizer (model MRE CN-24) purchased from BGI Inc. The compressed air system is allowed to operate at  $26.0 \pm 3.0$  °C and 23% relative humidity. The challenge stream generator provides an air stream at 5 L/min ( $83.5 \text{ cm}^3/\text{s}$ ) containing 800 ppm ( $8 \times 10^5 \text{ mg/m}^3$ ) of MeS. A cylinder of compressed air, that has been passed through an air filter, equipped with a two-stage regulator, is set to provide a feed pressure of 65 psi to the flow system. The compressed air flow is split and regulated by precision metering valves so that 3 L/min passes through the nebulizer containing MeS solution and 5 L/min by-passes the nebulizer and enters into the mixing chamber where vaporized MeS and by-pass streams are combined to generate the desired challenge gas mixture flow rate and MeS concentration under specified conditions. The influent air stream passes through the test material for a period of 30 minutes whereby the effluent air stream is directed to a trapping medium and subsequently, a UV-Vis absorption spectroscopy is used to determine the amount of MeS that has permeated through the prototype. The effluent samples were analyzed using the Ocean Optics UV-Spectrophotometer, model SD-2000 (acquisition enhanced UV resolution), and the lamp type utilized is the DT-1000 (Deuterium Tungsten-Halogen light source). A charged coupled device (2048 element linear CCD array detector) is used to detect the

signals. A quartz fibre optic dip probe (T300-RT-UV/VIS) is used to measure the concentration of MeS in the samples. This specific reflective probe has a total pathlength of 1 cm. Working at ambient temperatures, the detector is sensitive in the range of 200-800 nm. This is within the range of MeS detection. MeS has strong absorption peaks that occur at wavenumbers 236 nm and 302 nm. The absorption used for analysis is the peak at 302 nm. Effluent concentrations are extrapolated from calibration curves.

The breakpoint concentration, which determines service-life of the prototype, occurs when MeS concentration down-stream reaches 40 ppm ( $4 \times 10^4$  mg/m<sup>3</sup>, 5% of challenge concentration). The service-life measurements, in this research phase, will represent the physisorption capacity of the activated carbon.

The protocol for aerosol/vapor testing was extrapolated from TOP 8-2-501 entitled "Permeation and Penetration Testing of Air-Permeable, Semi-Permeable and Impermeable Materials with Chemical Agents or Simulants". The vapor testing station was specifically designed based on previous testing modules outlined in the DREO document #89-13 entitled "Apparatus and Methodology for Cyanogen Chloride Gas-Life Measurement of Gas-Mask Canisters" from National Defense Canada through the Defense Research Establishment Ottawa. This protocol describes the most recent apparatus and experimental procedure used to determine the absorption capacity of carbon/Triosyn-based hybrid materials as required by military specifications for the modified activated carbon. Adaptations of these protocols were essential in order to test according to set government standards and military specifications<sup>111213</sup>.

Microbiological efficacy: A tridimensional impregnation of the Triosyn® biocidal interactive polymer in a low pressure drop membrane and a separate impregnation of the new carbon based material provided a fraction of the pressure drop as compared to already marketed membranes. This produced a chemical and biological (C/B) prototype derived from a complex membrane whereby the first step provides the effective biocidal properties and the second step provides the enhanced absorption capabilities while allowing air stream velocity to be unhindered. Pressure drops were measured using U-tube manometer.

MS2 coliphage (ATCC 15597-B1), a bacterial virus known for its survival capacities in the environment, was used as a biological agent to challenge the different prototypes.

Different prototypes were tested in Aeromicrobiology Testing in order to assess the effectiveness of the treated filters in reducing a viral aerosol. Refer to system set-up in Figure I. The MS2 phage was diluted in DH<sub>2</sub>O and the solution placed in a 6 jet modified collision nebulizer. An air tank was used to pressurize the nebulizer and subsequently aerosolize the microbial suspension into the chamber. Different pre-vaporization times (0, 5, 15, and 30 minutes) were assayed at a rate of 10 LPM. Dilution air was added to the solution entering the chamber at a rate of 15 LPM. The airflow was distributed in the chamber with a built-in low speed fan and a vacuum pump ensured that it was passing through each filter unit with a velocity of 5 LPM. All experimental samples (carbon and PP3 Triosyn®) were embedded in a non-woven low quality/low pressure drop 95% of 0.3-micron retention material. The filter prototypes comprised three successive layers: non-woven with the chemical prototype, non-woven low quality / low pressure drop membrane (LPDM) and non-woven material impregnated with Triosyn® PP3. The filter prototypes were placed into BGI filter holders. Blanks were used for positive controls. These filter units were placed between the chamber and the sampling units (gelatine membrane filters placed into BGI filter holders). Filtration occurred for 15 minutes at 10 LPM and room temperature (approximately 20°C). Temperature and relative humidity (RH) were monitored at the beginning and at the end of each filtration run. Gelatin membranes were loaded in BGI filter holders. These collector units were placed after the test filter units. After filtration, gelatin membranes were placed in a 9 ml tube of neutralizing dilution solution buffer (NDS) kept in a 35°C water bath until complete dissolution of the membranes. Dilutions of MS2 assays were made in sterile PBS. Serial dilutions of the collection buffer (1ml) were plated in MS2 media and incubated at 35°C for 16-18 hours for subsequent enumeration of the number of PFU/ml.

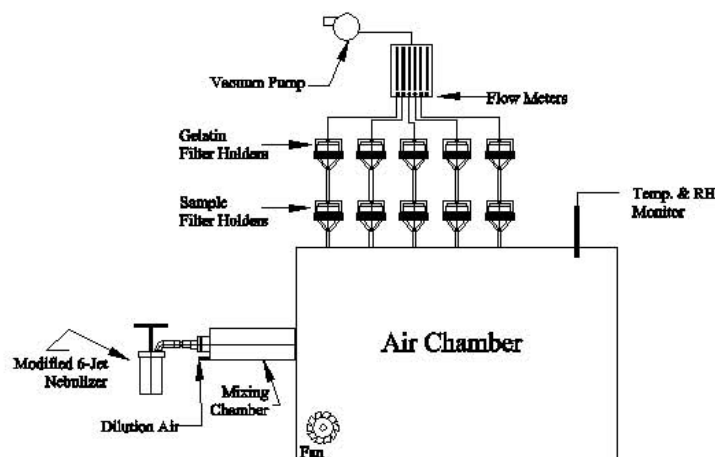


Figure 1. Aeromicrobiology testing chamber.

**Toxicology:** Experimental samples were tested to detect leaching of iodine content in the effluent air stream. An airflow passes through the air filter membrane samples allowing free particles to be transported into an AGI (all glass impinger) containing 100 ml of osmotic water. The duration of the test is 30 minutes at 30 L/min for a circular surface diameter of 4.5 cm. An aliquot of water from the glass impingers is sampled. Iodine testing must occur within 5 minutes of sampling. Total iodine content is measured with a spectrophotometer at a wavelength of 592  $\lambda$  for absorbance values.

The flow meter manufacturer provides correlation charts for positive pressures only. Consequently, the flow meters used in this experiment were calibrated for a vacuum environment, which differs from standard atmospheric conditions. Absorbance values measured with the spectrophotometer are converted first to ppm and then in mg/100ml. For a representative value of the effective surface of a human facemask, the values have to be converted in mg of iodine/100  $\text{cm}^2$  of tissue/ $\text{m}^3$  of air.

**Iodine method:** Mercuric chloride (Fisher Scientific) added to an aqueous elemental iodine solution results in complete hydrolysis of iodine and the stoichiometric production of hypoiodous acid. The compound 4,4,4 methylidynetris (N,N-dimethylaniline) (Leuco crystal violet, Aldrich #21,921-5) reacts with the hypoiodous acid to form crystal violet dye. The maximum absorbance the crystal violet dye solution produces in the pH range of 3.5-4.0 is measured at a wavelength of 592 nm. The absorbance follows Beer-Lambert's law over a wide range of iodine concentrations. Iodine can be measured in the presence of a maximum of 50 ppm iodide ions without interference.

**Total Iodine Method:** Iodide is selectively oxidized to iodine by the addition of potassium peroxymonosulfate (Oxone, Aldrich #22,803-6). The iodine produced reacts instantaneously with the indicator reagent Leuco crystal violet over the same conditions described previously for

iodine methods. Total iodine plus iodide is formed from this reaction and the iodide content is calculated from a subtraction of iodine concentration. Readings of absorbance have to be performed on a spectrophotometer with a pathlength of 1.0 cm set at a wavelength of 592 nm.

Prototypes tested: The investigations reported in this paper were conducted on two different types of activated carbon samples. Carbon in the form of Ambersorb 572 was used in the sphere, and particulate form and Nuchar (10-50  $\mu\text{m}$ ), for comparison to Ambersorb 572 in particulate form.

The quantity of spheres tested was set to form a monolayer of spherical carbon beads, similar to thin film coatings seen in textiles applications and testing. It is important to note that since we the samples were examined on a weight basis, for the quantities present of the prototypes, which contain a greater amount of oxygen molecules and impregnated material, the volume of prototype is generally less than that of the standard NATO carbon, Ambersorb 572.

## RESULTS AND DISCUSSION

The focus of phase I of CB-Materials research was to develop a new class of materials that have the capacity of adsorbing Chemical Warfare Agents in the vapor phase and retain the biocidal efficiency of the iodinated resin. The research in this phase was devoted to the synthesis of these new materials, and subsequent vapor testing with the mustard gas simulant MeS, the evaluation of microbiological activity of the selected prototypes and the toxicological assessment. The prototype materials underwent vapor testing against chemical warfare simulant MeS after the test materials were left at ambient temperature and 23% humidity for three days.

The UV-Vis absorption data presented in Table 1 is of effluent concentrations of MeS that has permeated through the prototype material from the vapor tests. MeS is collected in gas sampling impingers and detected by UV-Vis absorption spectroscopy. The testing station which is set-up to run a control, the standard carbon (in the form of Ambersorb 572 or Nuchar) and the prototype, allowed us to make an accurate comparison of prototype absorption efficiency of HD simulant MeS. The vapor testing protocol utilizes a high influent concentration, low air speeds and as a result, has allowed us to process a great number of prototypes for down-selection before decreasing the influent concentration of MeS and increasing air flows. The prototype OX5H/572 (carbon modified by surface oxidation) showed a significant improvement in vapor absorption with a 48% increase over Ambersorb 572. Another prototype, POX2/1/A572, which was synthesized using another surface oxidation technique, also resulted in an improved absorption of 26% over carbon spheres.

Combined technology: To further enhance the absorption capabilities of the carbon hybrid materials, a new class of prototypes was synthesized using a combination of synthetic methodologies from the polyoxometallate impregnation, nanoparticulate adsorbents and/or the oxidation of the carbon macrostructure. This novel synthetic methodology produced new materials, which result in a 10-20% increase in MeS vapor absorption over prototypes from previous carbon modifications. The carbon hybrid prototypes OX5H/D, OX5H/C, POX3/1/0/B and POX3/1/0/A result in MeS vapor absorption capacities of 67%, 59%, 54%, and 63% improvement over Ambersorb 572. The prototypes POX3/1/0/A, OX5H/C, and OX5H/D were down-selected for further studies.

TABLE 1. Vapor testing results for spherical beads.

Sample ID	MES concentration (ppm)						Absorption
	Avg. Control	Avg. A572	Avg. Prototype	Std. Control	Std. A572	Std. Prototype	Avg. %
POX2/1/A572	7.21	1.49	1.09	0.23	0.17	0.09	26%
OX5H/A572	6.07	1.94	0.99	1.10	0.45	0.51	48%
OX5H/D	6.92	1.84	0.61	0.93	0.43	0.20	67%
OX5H/C	6.79	1.71	0.73	1.85	0.71	0.22	59%
POX3/1/0/B	6.75	1.75	0.84	0.88	0.68	0.46	54%
POX3/1/0/A	7.24	1.60	0.61	1.44	0.90	0.36	63%

In order to further increase the absorption capacity of carbon, we examined particulate forms of carbon that originated from micronized Amborsorb 572 beads and Nuchar granules. This finely divided material imparts an increase in the surface area of the material. It was chemically modified as the spherical carbon beads. For the vapor tests, approximately 30 milligrams of the material was impregnated uniformly within a low-pressure drop membrane (LPDM). For the particulate samples, the above prototypes resulted in similar absorption capacities to the spherical carbon hybrids, with % MeS absorption of 57%, 58%, and 64%, for prototypes POX3/1/0/A, POX3/1/0/B and OX5H/D, respectively. The prototype OX5H/C showed a remarkable increase in MeS vapor absorption of 84% over micronized Amborsorb 572.

Of the prototypes selected, we undertook a study using Nuchar particulates functionalized similarly to Amborsorb 572. Vapor testing of the Nuchar-based prototypes POX3/1/0/A, POX3/1/0/B, OX5H/C and OX5H/D resulted in MeS absorption that ranged between 49%-60% better than Nuchar. Refer to Table 2.

TABLE 2. Comparative vapor testing results for particulates vs. Nuchar.

Sample ID	MES concentration (ppm)						Absorption
	Avg. Control	Avg. A572	Avg. Prototype	Std. Control	Std. A572	Std. Prototype	Avg. %
OX5H/C particulates	6.76	2.46	0.38	1.69	1.24	0.28	84%
OX5H/D particulates	6.23	3.17	1.14	1.52	1.23	1.13	64%
POX3/1/0/A particulates	5.62	2.29	1.12	1.05	0.98	1.09	57%
POX3/1/0/B particulates	5.29	2.15	0.91	1.03	1.05	0.61	58%
OX5H/C nuchar	5.66	1.76	0.79	0.47	0.39	0.18	55%
POX3/1/0/A nuchar	6.25	3.30	1.73	1.04	1.12	1.12	49%
POX3/1/0/B nuchar	8.02	4.48	1.82	0.77	1.47	1.12	60%
OX5H/D nuchar	5.44	1.72	0.78	0.75	0.95	0.78	55%

In order to investigate the absorption efficiency of beads versus particulate samples, we carried out a series of tests that examined the selected prototype being vapor tested simultaneously with both forms of carbon materials. The results presented in Table 3 suggest that the beads are about 42% better at absorbing MeS vapors. What is important to note, is that the quantity of beads present is *4 times greater* than the particulates, resulting in *only* a 1.5-fold increase in vapor absorption. This suggests that by doubling the quantity of particulates (60 milligrams), which is half the amount present for the beads (120 milligrams), the MeS vapor absorption would theoretically be similar. Further increases in the amount of particulates to 120 milligrams would subsequently result in drastic improvements over the modified beads. This study is still in its first phase, however, these preliminary results clearly suggest that the particulates have greater surface area than the beads and that far less material is required to perform better than the beads in MeS vapor absorption.

TABLE 3. Comparative vapor testing results for spherical beads vs. particulates.

Sample ID	MES concentration (ppm)						Absorption
	Avg. Control	Avg. Beads	Avg. Particulates	Std. Control	Std. Beads	Std. Particulates	Avg. %
OX5H/C	6.26	1.16	1.99	0.94	0.20	1.07	42%
OX5H/D	6.36	0.99	2.40	0.09	0.03	1.09	59%
POX3/1/0/A	7.68	1.21	2.73	0.90	0.34	1.12	56%
POX3/1/0/B	5.87	0.93	1.06	0.28	0.12	0.38	12%

Aeromicrobiology testing was conducted following the established protocol described above. CB prototype membranes produced reduction rates greater than 99.9% against MS2 phage at a concentration of  $10^9$  PFU/ml for all configurations involving prototypes from OXH and POX families Refer to Table 4.

TABLE 4. Filtration performances of C/B prototypes against MS2 phage.

First Run	PFU/ml	Reduction %
OX5H/D + Triosyn® PP3	1.05E+03	99.98
OX5H/D + Triosyn® PP3	8.60E+02	99.984
OX5H/C + Triosyn® PP3	4.70E+02	99.9913
OX5H/C+ Triosyn® PP3	1.64E+03	99.969
C+	5.40E+06	0

Initial Temperature & Relative Humidity 21.8°C & 18%

Final Temperature & Relative Humidity 23.3°C & 48%

Second Run	PFU/ml	Reduction %
POX 3/1/0 B + Triosyn® PP3	5.00E+02	99.99390
POX 3/1/0 B + Triosyn® PP3	4.30E+02	99.99476
POX 3/1/0 A + Triosyn® PP3	4.60E+02	99.9944
POX 3/1/0 A + Triosyn® PP3	1.70E+02	99.9979
C+	8.20E+06	0

Initial Temperature & Relative Humidity 21.8°C & 20%

Final Temperature & Relative Humidity 22.9°C & 52%



LPDM: Low pressure drop membrane

Parameters: challenge microorganism: MS2 phage; aerosol generated by: 6 jets modified collision nebulizer; air flow velocity: 5 LPM; nebulizer airflow: 10 LPM; dilution airflow: 10 LPM; orifice diameter: 4 cm; time: 15 min; pre-vaporization: 30 min; collection fluid: NDS; collection device: BGI holding a gelatine membrane; sampling on MS2 media by single layer soft agar.

TABLE 5. Efficacy of commercially available standard dust filter and Triosynated dust filter against MS2 phage @ 6 LPM.

Membrane	Äp (mm H <sub>2</sub> O)	PFU upstream	PFU downstream	% reduction
00315-3BM	38	2.70E+07	1.30E+04	99.952
Standard dust filter	1	3.40E+07	5.24E+06	84.590
Triosynated dust filter	1.5	3.40E+07	7.30E+01	99.999

Pressure drop readings showed commercially available filter papers having a pressure drop 25 times greater than Triosynated filter with less efficient percent reduction values. This provides a more efficient protective layer with a low pressure drop, thus minimizing the thermal load increase.

A toxicology evaluation was performed to ensure that the iodine gaseous/ particulate content leaching in the effluent air stream does not represent a health issue with regards to the use intended (face mask for individual protection). The total iodine content in ppm was determined following the established protocol described above. The values were then mathematically converted in Threshold Limit Values (TLV) to establish the toxicity level on a comparison basis using the following equation:  $\text{mg}/100\text{cm}^2/\text{m}^3 = (\text{mg}/\text{L}) \text{ iodine} \times 0,1\text{L} \times 100\text{cm}^2/\text{surf} (\text{cm}^2) \times (1000(\text{L}/\text{m}^3)/(\text{flow} (\text{L}/\text{min}) \times \text{time min}))$ .

As seen in Table 6, the TLVs established for selected prototypes were significantly below the acceptable standard of 1,0 mg/m<sup>3</sup> [ACGIH], 0,07 mg/m<sup>3</sup> being the highest value recorded.

TABLE 6. Toxicological evaluation.

CB Prototype	Total Iodine Absorbance (Average)	Free Iodine Absorbance (Average)	Total Iodine Concentration (ppm)	Free Iodine Concentration (ppm)	TLV (mg/m <sup>3</sup> )
OX5H/C + Triosyn® PP3	0.0035	0.0005	0.014	0.002	0.02
OX5H/D + Triosyn® PP3	0.005	0.001	0.048	0.004	0.05
POX3/1/0/A + Triosyn® PP3	0.0205	0.001	0.062	0.004	0.07
POX3/1/0/B + Triosyn® PP3	0.005	0.001	0.002	0.004	0.00

Parameters: material surface: 10.18 cm<sup>2</sup>; Air Flow: 30 liters/minute; Time: 30 minutes; Collector: AGI (all glass impinger); Spectrophotometer at 592nm  
LPDM: low pressure drop membrane

$$\text{Calculation: TLV (mg/100cm}^2\text{/m}^3\text{)} = [\text{iodine}] \text{ (mg/L)} * 0.1 \text{ L} * 100 \text{ (cm}^2\text{)} / \text{surface (cm}^2\text{)} * 1000(\text{L/m}^3) / \text{flow (L/min)} * \text{time (min)}$$

Where 100 cm<sup>2</sup> is the human facemask surface

The Threshold Limit Value is an exposition standard estimated for workers. Consequently, 40 hrs/week, 50 weeks/year and the average expected life span of an individual are the presupposed conditions of exposition. The utilization of a facemask for individual protection would imply a much smaller exposition factor.

## CONCLUSIONS

The prototypes resulting from nanoparticulate impregnation and surface oxidation and a combination of the various synthetic methodologies have resulted in improved efficiency in MeS vapor absorption. These technologies have produced new materials with enhanced capabilities at absorption of toxic vapors over the standard NATO carbon. Vapor testing using Nuchar-based carbon demonstrate similar results in MeS vapor absorption over Amborsorb 572-based materials. A comparative study of the vapor absorption of beads versus particulates suggests that the particulates present have a greater surface area of absorption than the beads. The C/B protective barrier was therefore lighter in weight and had a low pressure drop without toxic iodine gaseous/particulate content in the effluent air stream. The prototypes down-selected from the MeS vapor tests in the bead form are: POX3/1/0/A, OX5H/C, and OX5H/D and those prototypes selected from the particulates are: OX5H/C and OX5H/D.

In aeromicrobiology, excellent results were obtained with selected prototypes from OXH and POX families. Reduction rates greater than 99,9% against MS2 phage at a concentration of 10<sup>9</sup> PFU/ml were observed for all configurations.

The Threshold Limit Values established in the toxicology study for selected prototypes (OX5H/C, OX5H/D, POX3/1/0/A and POX3/1/0/B) were below the standard of 1,0 mg/m<sup>3</sup>, with the highest recorded value of 0.7 mg/m<sup>3</sup>. Therefore, the amount of iodine is significantly below the permissible levels that workers may be exposed to day after day without adverse effect.

## FUTURE WORK

In this research phase, our vapor testing conditions focused on utilizing high influent concentrations of the simulant compound and low air speeds similarly seen in vapor testing of textile materials. A direct examination of these new materials using lower challenge agent influent concentrations and higher air speeds is essential in order to examine the rate of simulant absorption in the vapor phase as well as gain an understanding of the diffusional effects of the material. Reproducibility of the down selected prototypes will undergo testing to assess any loss of efficacy over time. We are also continuing work on improving the detection limits of the UV-Vis spectrophotometer and this will allow us to increase the detection limits to low ppb and subsequently allow testing to occur using lower influent concentrations and higher air speeds This research study has focused on the absorption properties using HD simulant MeS. Our lab designed and synthesized these new carbon-based materials with the potential to catalytically destroy chemical agents and simulants. Key issues to be addressed are the breakdown products

formed and the materials' capacity to absorb these contaminants. These new materials may impart beneficial characteristics in terms of catalyst activity and selectivity as well as contribute advances in tailor-made CW reactive absorbents and biocidal products.

## REFERENCES

- 
- <sup>1</sup> **Bandosz, T.J.** 1999. *Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfide.* Carbon, 37, 483-491.
  - <sup>2</sup> **Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Orfao, J.J.M.** 1999. *Modification of the surface chemistry of activated carbons.* Carbon, 37, 1379-1389.
  - <sup>3</sup> **Xie, F., Phillips, J., Silva, I.F., Palma, M.C., Menendez, J.A.** 2000. *Microcalorimetric study of acid-sites on ammonia- and acid-pretreated activated carbon.* Carbon, 38, 691-700.
  - <sup>4</sup> **Mochida, I., Korai, Y., Shirahama, M., Kawano, S., Hada, T., Seo, Y., Yoshikawa, M., Yasutake, A.** 2000. *Removal of SO<sub>x</sub> and NO<sub>x</sub> over activated carbon fibers.* Carbon, 38, 227-239.
  - <sup>5</sup> **Raymundo-Pinero, E., Cazorla-Amoros, D., Salinas-Martinez de Lecea, C., Linares-Solano, A.** 2000. *Factors controlling the SO<sub>2</sub> removal by porous carbons: relevance of SO<sub>2</sub> oxidation step.* Carbon, 38, 335-344.
  - <sup>6</sup> **Stark, J.V., Park, D.G., Lagadic, I., Klabunde, K.J.** 1996. *Nanoscale metal oxide particles/clusters as chemical reagents. Unique surface chemistry on magnesium oxide as shown by enhanced adsorption of acid gases (sulfur dioxide and carbon dioxide) and pressure dependence.* Chem. Mater., 8, 1904-1912.
  - <sup>7</sup> **Wagner, G.W., Bartram, P.W.** 1995. <sup>31</sup>P MAS NMR study of the hydrolysis of O,S-diethylphenylphosphonothioate on reactive sorbents. Journal of Molecular Catalysis A: Chemical, 99, 175-181.
  - <sup>8</sup> **Wagner, G.W., Bartram, P.W.** 1995. <sup>31</sup>P MAS NMR study of the hydrolysis of O,S-diethylphenylphosphonothioate on reactive sorbents. Journal of Molecular Catalysis A: Chemical, 99, 175-181.
  - <sup>9</sup> **Wagner, G.W., Bartram, P.W., Koper, O., Klabunde, J.** 1999. *Reactions of VX, GD, and HD with Nanosize MgO.* Journal of Physical Chemistry, 103, 3225-3228.
  - <sup>10</sup> **Yang, Y.C., Baker, J.A., Ward, J.R.** 1992. *Decontamination of Chemical Warfare Agents.* Chem. Rev., 92, 1729-1743.
  - <sup>11</sup> **Liang, S.H.C., Poirier, R.T., Harrison, B.H.** 1989. Technical Note 89-13 *Defence Research Establishment Ottawa. Apparatus and methodology for cyanogen chloride gas-life measurement of gas-mask canisters*

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<sup>12</sup> **Campbell, L.E., Pappas, A.G.** 1999. ERDEC-TR. *Domestic preparedness: Sarin vapor challenge and corn oil protection factor (PF) testing of powdered air purifying respirator (PAPR) systems and cartridges.*

<sup>13</sup> **Commander U.S. Army Dugway Proving Ground.** 1997. TOP 8-2-501. Permeation and penetration testing of air-permeable, semi-permeable and impermeable materials with chemical agents or simulants (swatch testing).